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(54) Optical device.

(57) Optical devices such as optical disk substrates and lenses are prepared by molding a resin composition comprising 100 parts by weight of a mixture of 30 to 70% by weight of a polymer in which 50% by weight or more is composed of aromatic vinyl monomer units and 70 to 30% by weight of a polyphenylene ether, and 0.005 to 2 parts by weight of an organic carboxylic acid.

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OPTICAL DEVICE

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to small-birefringent optical devices which are useful, for example, as optical disk substrates for recording and reproducing information optically, lenses, prisms, etc.

2. DESCRIPTION OF THE PRIOR ARTS

Recently there is noticed the system of recording and reproducing high-density information, e.g. images and/or sounds, by using laser beams, wherein the information is recorded in the form of fine projections or depressions on disk substrates or in the form of changes in an optical property of recording films formed on disk substrates.

Disk substrates for use in the above recording and reproducing system are required to be transparent and in addition have such properties as good dimensional stability, high optical homogeneity, and small birefringence.

A plenty of duplicated substrates can be economically produced by using a resin material as a material of the disk substrate. However, it is widely recognized that the resin flows during the molding of the disk substrate and molecules are oriented during cooling so that birefringence is induced. This is a fatal defect for optical disk substrates.

The molecular orientation caused during molding is inevitable particularly in injection molding. From these point of view, a polymer comprising methyl methacrylate is the only resin material with small optical anisotropy for molding of disk substrates.

Known polymer comprising methyl methacrylate, however, have a drawback in that because of their high hydroscopicity, substrates formed thereof are inferior in dimensional stability, that is, the substrate warps and/or twists in high humid atmosphere.

This drawback is as described in detail, for example, in Nikkei Electronics (p. 133, issued June 7, 1982). Therefore, aromatic polycarbonate resins having low hygroscopicity are in use as materials for acoustic compact disks.

On the other hand, it is difficult to decrease the birefringence of the molded substrates formed of aromatic carbonate resins since they contain aromatic rings, which have large anisotropy, in the backbone chain. While decreasing of the molecular weight and conditions of the molding are under investigation. However, since birefringence of the substrate originates from the material itself, it is impossible to constantly produce substrate with small birefringence and it is extremely difficult at present to produce small-birefringent substrates larger in diameter than acoustic compact disk by injection molding.

To improve dimensional stability which is a drawback of the polymer comprising methyl methacrylate, copolymers comprising methyl methacrylate and aromatic vinyl monomer are proposed [e.g. Japanese Patent Application (Laid-Open) Nos. 33446/82, 162135/82, and 88843/83]. However, these copolymer having aromatic rings cannot be practical use on account of their liability to large birefringence. For the disk substrates which is used not only for reproducing but also recording of information, a material is required to have further small birefringence and dimensional stability, but no resin has yet been found out that can enough satisfy these requirements.

With respect to other optical devices including lenses and prisms, for which methacrylic resins and the like have been used as materials, there are needs for optical devices formed from a resin which is further small birefringence and superior in heat resistance, mechanical strength, and dimensional stability.

U.S. Patent No. 4,373,065 discloses an optical recording device comprising an optically isotropic composition prepared by mixing two resins which have opposite optical anisotropies but are completely miscible with each other, in such a ratio that their optical anisotropies will be just compensated with each other to reduce the birefringence to substantial zero.

This patent further describes mixtures prepared by using a polyphenylene ether and polystyrene as component polymers having opposite optical anisotropies and showed that a film prepared such a

composition of the mixtures that these anisotropies are just compensated with each other does not cause birefringence even when stress is exerted on the film in the solid state.

However, this patent does not reveal that an optical device such as an optical disk substrate, when formed from the above polymer composition by injection molding, exhibits small birefringence.

The present inventors have found that the birefringence of moldings such as optical disk substrates is not always small when these moldings are formed by injection molding, which is recently the most common method of forming optical devices, even from a mixture of two polymers which have opposite optical anisotropies in the solid state but are completely miscible with each other, wherein the mixing ratio is such that the optical anisotropies in the solid state are just compensated with each other.

That is, it has been found that optical materials such as an optical disk substrate having small birefringence can not be obtained by injection molding of any composition of polymer mixtures that is chosen by considering merely the optical anisotropy of each polymer in the solid state.

In recent years, attemps are in progress to produce plastic substrates of magneto optical disks where the erasing and rewritting of information are possible.

Information recorded on such an optical disk of a magneto optical type is read by focussing a polarlized laser beam through a lens on the recording medium of the disk and detecting a Kerr effect-induced slight rotation of the polarization plane of the laser beam reflected from the recording media. Accordingly, it is necessary in this case to use an optical disk substrate which scarcely causes the birefringence for oblique incident beams as well.

In addition, the optical disk substrate is required the high heat resistance since the substrate during information writting is heated by a laser beam.

Furthermore, from the viewpoint of environmental stability, the adherence of a recording medium and an optical disk substrate should be excellent for a long period of time.

SUMMARY OF THE INVENTION

The view of such circumstances as stated above, the present inventors made intensive studies, and as a result have been successful in providing an optical device which has small birefringence for vertical incident beams as well as oblique them even when formed by injection molding, compression molding, or the like, and has high heat resistance, well-balanced mechanical strengths, and superior dimensional stability, and excellent adhesion to recording medium for a long period of time.

According to the present invention, there is provided an optical device comprising polymer portions constituted mostly of aromatic vinyl monomer units and polyphenylene ether portions, and an organic carboxylic acid.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to optical devices comprising 100 parts by weight of a mixture of 30 to 70% by weight of a polymer in which 50% by weight or more is composed of aromatic vinyl monomer units, 70 to 30% by weight of a polyphenylene ether, and 0.005 to 2 parts by weight of an organic carboxylic acid.

The polymer in which 50% by weight or more is composed of aromatic vinyl monomer units, referred to in the invention, is an aromatic vinyl homopolymer or a copolymer comprising aromatic vinyl monomer units in an amount of at least 50% by weight. Examples of the aromatic vinyl monomer include styrene, α-methylstyrene, m-methylstyrene, p-methylstyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, m-bromostyrene, and p-bromostyrene. In particular, styrene is favorably used.

Suitable monomers herein for copolymerization with such an aromatic vinyl monomer include; unsaturated nitriles, e.g. acrylonitrile and methacrylonitrile; alkyl methacrylates, e.g. methyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, and cyclohexyl methacrylate; alkyl acrylates, e.g. methyl acrylate, ethyl acrylate, propyl acrylate, and butyl acrylate, and further, methacrylic acid, acrylic acid, maleic anhydride, citraconic anhydride, N-methylmaleimide, and N-phenylmaleimide.

These comonomers may be used alone or in combination, wherein the kinds and proportions of monomers used may be suitably chosen within the range ther of where none of them impair the transparency of the resulting polymer composition that comprises an aromatic vinyl copolymer and a polyphenylene ether.

The proportion of the aromatic vinyl monomer in the monomer mixture to form the copolymer is desired

to be at least 50% by weight, otherwise the resulting resin will have undesirably high hygroscopicity.

The melt fluidity of the polymer constituted mainly of aromatic vinyl monomer units, expressed in melt flow rate (MFR) at 230°C under 3.8 kg load, is desirably from 0.5 to 200, preferably from 2 to 100. When the MFR exceeds 200, the polymer is poor in mechanical strength and when the MFR is less than 0.5, the birefringence is difficult to decrease.

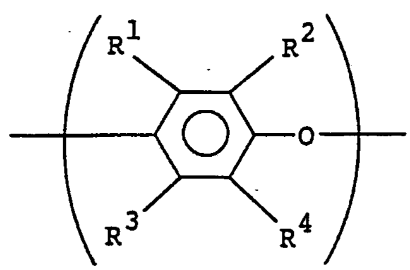
The polymer constituted mostly of aromatic vinyl monomer units may be produced by any of bulk, suspension, emulsion, and solution polymerization methods using a radical initiator, but bulk polymerization and suspension polymerization are preferable in view of the productivity and less impurity-contamination of the polymer.

Suitable radical initiators for the polymerization include peroxides, e.g. lauroyl peroxide, benzoyl peroxide, di-tert-butyl peroxide, and dicumyl peroxide, and azo compounds, e.g. 2,2′-azobisisobutyronitrile and 1,1′-azobis(1-cyclohexanecarbonitrile).

If necessary for controlling the molecular weight, such a chain transfer agent is added as tert-butyl, n-butyl, n-octyl, n-dodecyl, or tert-dodecyl mercaptan.

The polymerization is generally carried out at a temperature of 50 to 150°C.

The polyphenylene ether referred to in the present invention is a polymer consisting of recurring units represented by the formula



wherein each of R^1, R^2, R^3 and R^4 denotes hydrogen, halogen, or hydrocarbon groups.

Polyphenylene ethers, defined above, are readily prepared by known methods (see, e.g. Japanese Patent Publication Nos. 18692/61 and 36518/72), that is, by oxidative coupling of phenolic monomers in the presence of a copper or manganese catalyst.

Examples of the polyphenylene ethers include poly(2,6-dimethyl-1,4-phenylene) ether, poly(2-methyl-6-ethyl-1,4-phenylene) ether, poly(2-methyl-6-propyl-1,4- phenylene)ether, poly(2,6-dipropyl-l,4-phenylene)-ether, and poly(2-methyl-6-bromo-l,4-phenylene)ether. In particular, poly(2,6-dimethyl-l,4-phenylene)ether is preferable.

In the present invention, polyphenylene ether resins generally in use as engineering plastics are acceptable but those of lower molecular weights are preferred.

That is, when the average molecular weight of polyphenylene ether is expressed in terms of the intrinsic viscosity of the polymer in chloroform at 25°C, acceptable values thereof are 0.1 to 1.0, but desirable are 0.3 to 0.7, preferable 0.3 to 0.4.

When the value is less than 0.1, the resulting optical device will have poor mechanical strength and will not have small birefringence. When the value is more than 1.0, not only the homogeneity but also the melt flow rate of the molding composition are lowered.

The organic carboxylic acid for the present invention includes aliphatic carboxylic acids, alicylic carboxylic acids, and aromatic carboxylic acids. The aliphatic carboxylic acids include aliphatic monocarboxylic acids such as butyric acid, valeric acid, hexanoic acid, stearic acid, and the like; and aliphatic dicarboxylic acids such as malonic acid, succinic acid, methylmalonic acid, ethylmalonic acid, methylsuccinic acid, glutaric acid, adipic acid and the like. The aromatic carboxylic acids include benzoic acid, o-methylbenzoic acid, m-methylbenzoic acid, p-methylbenzoic acid, o-, m- and p-ethylbenzoic acid, o-, m- and p-hydroxybenzoic acid, o-, m- and p-phthalic acid, phenylmalonic acid, trimesic acid, pyromellitic acid, salicylic acid, 3,4-dimethoxybenzoic acid, 3,5-dimethoxybenzoic acid, m- and p-methoxybenzoic acid, m-, p- and t-butylbenzoic acid, 2-phenoxybenzoic acid, 3,5-di-t-butyl-4-hydroxybenzoic acid, biphenyl-2,2′-dicarboxylic acid, 4,4′-bis(p-hydroxyphenyl)valeric acid, mandelic acid, etc. Among them, the aromatic carboxylic acids are preferred.

In the present invention, melt or solution mixing is suitable for preparing the resin material of optical devices by mixing the aromatic vinyl-based polymer and the polyphenylene ether and the organic

carboxylic acid.

The melt mixing is carried out by using a mixing machine such as an extruder, Banbary mixer, kneader blender, or heat roller mill under high shear stress at temperatures of at least the glass transition point of the polyphenylene ether.

The degree of mixing is such that particles sizes of both the mixed and dispersed polymers become desirably about 1 μ or less, preferably of molecular order. Whether the molecular-order dispersion is reached can be readily judged by observing the mixture to exhibit a single glass transition temperature.

For achieving the much satisfactory state of mixing, the means are taken of raising the mixing temperature, extending the mixing period, and further enhancing the shear stress.

In the melt mixing, an organic solvent may be used in a small amount as a plasticizer for lowering the glass transition temperature of both the polymers, thereby facilitating the mixing.

Organic solvents, as cited below, suitable for the solution mixing can also be used in this case. The used solvent may be removed by distillation after completion of the mixing.

The solution mixing can be accomplished by dissolving each polymer in an organic solvent to a concentration of at least 1% by weight, mixing the solutions with stirring to form a uniform mixture, and either distillation of the mixture to remove the solvent or addition of a solvent poor in the ability to dissolve both the polymers to the mixture to precipitate the polymers.

Suitable solvents for the solution mixing include, for example, chloroform, toluene, benzene, and chlorobenzene. Suitable poor solvents include, for example, methanol, ethanol, propanol, n-hexane, and n-pentane, etc.

The proportions of the aromatic vinyl-based polymer and the polyphenylene ether, in the optical device, are 30 - 70%, preferably 40 - 55%, by weight and 70 - 30%, preferably 60 - 45%, by weight, respectively. When the proportion of the polyphenylene ether is less than 30% by weight or more than 70% by weight, the birefringence of the optical-device is not sufficiently small. In addition, when the polyphenylene ether proportion is less than 30% by weight, the optical device is insufficient for heat resistance.

The proportion of the organic carboxylic acid is 0.005 to 2 parts by weight, preferably 0.01 to 1 parts by weight per 100 parts by weight of the resin. When the proportion is less than 0.005 parts by weight, the environmental stability of the optical device of the present invention is not sufficient particularly when the optical device is used as an optical disk substrate. When the proportion exceeds 2 parts by weight, not only the heat resistance but also the transparency are lowered.

The resin composition of the optical device, in practice, is suitably chosen within the above defined range depending on the method of molding. In injection molding, for example, the resin proportions may be suitably chosen depending on preset conditions of molding, such as resin temperature, injection pressure, and mold temperature so that the birefringence of the moldings will agree with the level required to use the product for the intended purposes.

Optical devices, particularly optical disk substrates, of the present invention in certain applications transmit semiconductor laser beams or the like. Accordingly, the light transmittance of optical devices for such applications is desired to be at least 75% at a wavelength of 800 nm when the thickness of optical device is 1.2 mm.

Of the optical devices of the present invention, optical disk substrates can be formed by injection molding, compression molding, and injection-compression molding. The effect of the present invention is the more remarkable when a molding method, among the above, is applied that tends to form the higher birefringent products, though injection molding is best suited in view of productivity.

The optical devices according to the present invention show small birefringence even when they are produced by injection molding, compression molding or the like. Moreover, they show only small birefringence even in the case of an oblique incident beam, and have high heat resistance, well-balanced mechanical strength, and excellent dimensional stability.

Furthermore, when used as a substrate for magneto optical disk, the optical device according to the present invention has excellent adhesive properties to recording medium and excellent environmental stability. Thus, it can be said that the present invention is very effective for cost reduction and general application as magneto optical disk.

The following examples illustrate the present invention in more detail without limiting the scope of the invention. In the examples, parts and percentages are all by weight.

Physical properties shown in the examples wer measured in the following ways. o Intrinsic viscosity of polymer:

Measured in chloroform at 25°C using Ubbelohde viscometer, followed by calculation.

o Water absorption:

Equilibrium water absorption in water at 60°C was measured in accordance with ASTM D-570.

o Light transmittance:

Th transmittance of a 1.2 mm thick specimen was measur d at a wavelength of 800 nm using a self recording spectrophotometer (Model 330, mfd. by Hitachi Ltd.) o Flexural properties:

Measured in accordance with ASTM D-790. o Heat resistance:

Expressed in terms of glass transition temperature measured by the linear expansion coefficient method by the use of a 5 mm x 5 mm x 3 mm test piece.

o Birefringence:

Retardation was measured at 546 nm according to the Cénarmont compensator method by means of a polarization microscope.

o Evaluation of performance characteristics of magneto optical disk:

Heat history conditions of magneto optical disk:

Humidity : 93 ±3% constant
Temperature change: 1 cycle 24 hours

Temperature (°C)	Time
25	2.0
25 → -10	0.75
-10	2.75
-10 → 25	0.5
25	1.0
25 → 65	1.5
65	5.0
65 → 2.5	1.5
25	1.0
25 → 65	1.5
65	5.0
65 → 25	1.5

Conditions of recording on magneto optical disk:

Rotation rate: 1800 r.p.m.
Recording frequency: 1 MHz (for C/N)
3 MHz (for BER)

Recording power: 6 mW
Recording magnetic field: 350 Oe
Recording time: 10 s conds (for about 300 tracks)

C/N:

Measured at a position of 30 mm distance from the center of the disk by using a magneto optical disk evaluating apparatus OMS-1000 mfd. by NAKAMICHI CO.

Bit error rate (BER):

Measurement was conducted at a reproducing output of 1 mW at positions of 40 mm, 45 mm, 50 mm and 55 mm disk radii by using the same apparatus as described above, and the average value was calculated.

State of recording medium:

Confirmed by visual observation.

o The kneading and pelletizating was carried out by using a twin-screw extruder (Model TEX30-30BW-2V, supplied by the Japan Steel Works, Ltd.).

o The injection molding was carried out by using an injection molding machine (Neomat Model 150/75 (75 ton), supplied by Sumitomo Heavy Industries, Ltd.) and a mold for producing a disk 130 mm across and 1.2 mm thick.

Example 1

In a 2 m^3 reactor equipped with a thermometer, reflux condenser, dropping funnel, stirrer, and gas inlet tube was placed a mixed solution of 2.2 kg of ethanolamine and 10 kg of methanol, and stirred. Subsequently, 64 kg of a solution of 30 g of manganese (II) chloride dissolved in methanol and 254 kg of xylene were placed in the reactor, and oxygen gas was passed through the reactor for 15 minutes. Then, a mixed solution of 98 kg of 2,6-xylenol and 120 kg of xylene was charged into the reactor, after which oxygen gas was blown through the resulting mixture with stirring to subject the mixture to reaction at 30°C for 5 hours. The reaction mixture was poured into a large amount of methanol containing a small amount of hydrochloric acid to precipitate a polymer. The polymer was filtered and the residue was washed with methanol and water and dried to obtain 92 kg of poly(2,6-dimethyl-l,4-phenylene) ether having an intrinsic viscosity of 0.40.

With 50 kg of the polyphenylene ether were mixed 50 kg of polystyrene resin (ESBRIGHT® 4-62A, mfd. by Sumitomo Chemical Co., Ltd.) and 1 kg of m-phthalic acid (mfd. by Wako Pure Chemical Industries Ltd.), followed by kneading and granulation by means of an extruder.

By the use of a part of the pellets thus obtained, the light transmittance, water absorption rate, flexual properties and heat resistance were measured. The results obtained are shown in Table 1.

Further, the pellets were injection-molded at a cylinder temperature of 320°C and at a mold temperature of 85°C to obtain a grooved substrate (groove pitch: 1.6 µ) having a diameter of 130 mm and a thickness of 1.2 mm.

The birefringence was measured at 35 mm distance from the center of the disk substrate. The result obtained is shown in Table 1.

Reactive sputtering of silicone was conducted on the substrate in an atmosphere of mixed gas of argon and nitrogen under a vacuum of 5 x 10^{-3} Torr to form a silicon nitride film having a refractiv index of 2.0 and a thickness of 850 Å.

Further, in accordance with the conventional method, magnetic layer of TbFeCo was sputtered on the silicon nitride film to a thickness of 900 Å, followed by sputtering thereon silicon nitride to a thickness of

850 Å in the same manner as described above, whereby a magneto optical disk having a structure of substrate silicon nitride/TbFeCo/silicon nitride was prepared.

Performance characteristics of the magneto optical disk were evaluated. The results obtained are shown in Table 1.

Example 2

The process of Example 1 was repeated except for changing the amount of m-phthalic acid from 10 g to 1 kg. The results obtained are shown in Table 1.

Example 3

The process of Example 1 was repeated except for using 100 g of p-phthalic acid in place of 1 kg of m-phthalic acid. The results obtained are shown in Table 1.

Example 4

The process of Example 1 was repeated except for using 200 g of trimesic acid in place of 1 kg of m-phthalic acid. The results obtained are shown in Table 1.

Comparative Example 1

The process of Example 1 was repeated without m-phthalic acid. The results are shown in Table 1.

Comparative Example 2

The process of Example 1 was repeated except for changing the amount of m-phthalic acid from 1 kg to 3 kg. Bleeding of a large amount of m-phthalic acid was observed on a substrate obtained by injection molding, and the subsequent evaluation was impossible.

Comparative Example 3

The process of Example 1 was repeated except for changing th amount of m-phthalic acid from 1 kg to 2 g. The results obtained are shown in Table 1.

Table 1

	Properties			Example 1	Example 2	Example 3
Resin composition	Light transmittance (%)			87	87	87
	Water absorption (%)			0.11	0.11	0.10
	Flexural strength (kg/cm^2)			980	1010	1000
	Heat resistance (°C)			145.1	146.0	145.8
Substrate	Retardation (nm)			-2.0	-1.5	-1.5
Magneto optical disk	Heat history	Before	C/N (dB)	46	46	46
			BER	$7.9x10^{-5}$	$7.9x10^{-5}$	$7.8x10^{-5}$
			State of recording medium	-	-	-
		After once	C/N (dB)	46	46	46
			BER	$8.1x10^{-5}$	$8.2x10^{-5}$	$8.0x10^{-5}$
			State of recording medium	Unchanged	Unchanged	Unchanged
			C/N (dB)	46	46	46

- cont'd -

Table 1 (cont'd)

		After 10 times	BER	8.2×10^{-5}	8.5×10^{-5}	8.3×10^{-5}
			State of re-cording medium	Unchanged	Unchanged	Unchanged
		After 30 times	C/N (dB)	45	45	45
			BER	8.2×10^{-5}	8.6×10^{-5}	8.5×10^{-5}
			State of re-cording medium	Unchanged	Unchanged	Unchanged

- cont'd -

Table 1 (cont'd)

Example 4	Comparative Example 1	Comparative Example 3
87	88	88
0.10	0.10	0.10
1020	1060	1050
145.5	146.8	146.5
-1.0	+2.0	-1.5
46	46	46
$7.8x10^{-5}$	$7.8x10^{-5}$	$7.9x10^{-5}$
-	-	-
46	46	46
$8.1x10^{-5}$	$3.1x10^{-4}$	$3.4x10^{-4}$
Unchanged	Unchanged	Unchanged
46	45	45

- cont'd -

Table 1 (cont'd)

$8.5x10^{-5}$	$9.2x10^{-4}$	$9.0x10^{-4}$
Unchanged	Unchanged	Unchanged
45	40	41
$8.7x10^{-5}$	$2.4x10^{-3}$	$3.5x10^{-3}$
Unchanged	Bubble-like peeling	Bubble-like peeling

Claims

1. A composition for the manufacture of optical devices comprising 100 parts by weight of a mixture of 30 to 70% by weight of a polymer in which 50% by weight or more is composed of aromatic vinyl monomer units and 70 to 30% by weight of a polyphenylene ether, and 0.005 to 2 parts by weight of an organic carboxylic acid.

2. The composition of Claim 1, wherein the organic carboxylic acid is an aromatic carboxylic acid.

3. The composition of Claim 2, wherein the aromatic carboxylic acid is m-phthalic acid or trimesic acid.

4. A low-birefringency optical device formed from a composition according to any of claims 1 to 3.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 5463

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,Y	EP-A-0 225 801 (SUMITOMO) * Claim 1; page 6, lines 15-20,21-25; page 7, lines 1-25; page 13, lines 7-17 *	1	C 08 L 25/04 C 08 L 71/04 G 02 B 1/00 // (C 08 L 25/04 C 08 L 71:04) (C 08 L 71/04 C 08 L 25:04)
Y	PATENT ABSTRACTS OF JAPAN, vol. 10, no. 131 (C-346)[2188], 15th May 1986; & JP-A-60 258 253 (MITSUBISHI)	1	
D,Y	US-A-4 373 065 (W.M. PREST) * Claims 1-5 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08-10-1990	DEPIJPER R.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EUROPEAN PATENT REGISTRATION

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Planiform optical laser recording.

Planiform optical laser recording with

(B) an amorphous, electrically conductive, thermally modifiable recording layer with

(b_1) 30 to 95% by weight with respect to (B) of a cationic polymer, producible by electrolysis and

(b_2) 5 to 70% by weight with respect to (B) of an anionic pigment on one side or on both sides of an

(A) electrically conductive, dimensionally stable carrier in the form of

(a_1) a band, a quadratic or a rectangular plate or a round disc made from plastic,

in which

(a_2) the surface of the carrier (A) , which is turned to a recording layer (B), is structured and moreover

(a_3) covered by a 20 to 100 nm thick metal layer, as well as a process for the production of the recording material and a process for optical laser writing and reading of data.

Planiform optical laser recording

The invention concerns a planiform optical laser recording with

(A) an electrically conductive, dimensionally stable carrier and with

(B) one or two amorphous, electrically conductive, thermally modifiable recording layer(s) lying facing each other with a cationic polymer, producible by electrolysis, as one of the essential components.

The term "planiform" refers, in this case, to all spatial forms whose thickness is considerably less than its length and breadth. Therefore, it comprises recording materials in the form of band, plate, or disc, in which the disc forms are also called optical data plates.

The term "amorphous" indicates that the material of the recording layer (B) has no crystalline regions that are larger than the thermally modified areas, but is physically isotropic for this order of magnitude.

The designation "thermally modifiable" refers to regions with changed optical properties that are formed in the recording layers (B), by radiation of a writing laser ray focussed on it at the target areas. It could concern holes, craters or spots of new material modifications at these areas. If holes are formed with the laser radiation, one speaks generally of ablative recording, if craters are formed with it, one calls it

generally deformative recording, and if new material modifications are formed with it, then this is also designated as recording by phase change.

Here, only such materials that show conductivity δ of more than 10^{-2} s/cm are regarded as "electrically conductive".

Planiform optical laser recording with recording layers that contain pigments and polymers are known from US-A-4 529 688, EP-A-0 OREP-A-0 171 045.

The pigments can be present in the recording layers of EP-A-0 182 946 as components of the main chain of polymers. Therefore, they are combined covalently with polymers.

On the other hand, the recording layers of EP-A-0 171 045 contain pigments as covalently combined side-groups of polymers.

In addition to that, recording layers from EP-A-198 140 are known, whose metal containing pigments are linked with the polymers via the metals.

Recording layers of this type are in general produced by depositing solutions of the layer-components on carriers and evaporating the solvent (liquid coating) and are not electrically conductive.

The disadvantage in this case is that the respective pigments used exhibit in the solid state only limited solubility in or compatibility with the polymers, so that they crystallise very readily, especially in the high concentrations required for optical laser recording layers in which the layers become inhomogeneous and are no longer suitable for data recording.

One can overcome this disadvantage by combining the pigments with the polymers covalently or via metals. Thereby, the pigments can be components of the polymer main chain or be present as side groups. In both the cases, the pigments to be used are

such, they are not obtainable readily but are especially synthesised only for the corresponding application purpose and then must be further processed into polymers, or the polymers have to be modified afterwards by polymer-analogous conversion with pigments. However, all these are also disadvantageous.

Irrespective of what type a known pigment-polymer combination is, it can in general be applied on the carrier only by liquid coating. However, the disadvantage with the liquid coating is with regard to exact adjustment and reproducibility of the thickness of the recording layer. In particular, it permits hardly any correction during coating. Most of the solvents required for the liquid coating cause ecological problems and technical problems in processing. Besides, holes or cracks can be formed in the layers when the wet layers dry, making the layers unusable for optical laser data recording. The reasons for the disadvantages of liquid coating can be overcome to a certain extent by the electrolytic precipitation of amorphous, electrically conducting, thermally modifiable recording layers (B) on electrically conductive, dimensionally stable carriers (A).

Thus, e.g., a planiform optical laser recording is known from JP-A-61 143 192 (Priority JP 84 265 457 of 18.12.84), whose recording layer (B) is precipitated from a solution of pyrrole, thiophene, furan, indole or azulene in water, acetonitrile or ethanol (= electrolyte) on a carrier (A) of Au, Ni, Si or metallic oxide like indium oxide electrolytically. The electrolyte, moreover, can contain potassium chloride, tetra-n-butylammonium perchlorate and pigments.

Besides, from the lecture of W. Gambogi, L. Traynor and E. Buhks during the optical data storage conference at Lake Tahoe, 1987, U.S.A, abstract no. FA5-1, "Conductive polymers as active optical storage media", a recording material is known whose recording layer (B) is precipitated made from polypyrrole on a carrier (A) on glass, which is electrolytically covered with an electrically conducting oxide.

Further, from the article of M.V. Rosenthal, T.A. Skotheim and C.A. Linkous, "Polypyrrole-phthalocyanine", in Synthetic Metals, volume 15, pages 219 to 227, 1987,

it is known how to produce polypyrrole-phthalocyanine layers made from electrolytes, which contain phthalocyanine containing pyrrole and sulphonate groups, on platinum- or indium-tinoxide electrodes. It cannot be gathered from the article whether these layers come into question as recording layers (B).

Although the known planiform optical laser recording, whose recording layers (B) have been produced electrolytically, can remove the disadvantages of the liquid coating to a certain extent, there are additional disadvantages in this case:

As yet, only the named carrier materials come into consideration for the production of the known planiform optical laser recording. But, carriers (A) of this type are only of limited use in planiform optical laser recording. Besides, the known planiform optical laser recording often exhibits a strongly varying signal-to-noise ratio for the same combination and thickness of the recording layer (B). On top of this, the retracing of written data is frequently and unpredictably disturbed, i.e. the so-called "tracking" behaviour of the recording materials is hardly satisfactory and is not sufficient for the procedure, for which faster access to the data is essential.

The task of the present invention is to find new planiform optical laser recording materials with

(A) an electrically conductive, dimensionally stable carrier and with

(B) one or two amorphous, electrically conductive, thermally modifiable recording layer(s) facing each other with a cationic polymer, which can be produced by electrolysis, as one of the essential components

which does not have the disadvantages of the present technology. Beyond that, the new recording materials should exhibit, both in the written as well as in the unwritten condition, high storage stability so that the signal-noise-ratio does not deteriorate

during storage and no information is thereby lost. Besides, it should exhibit good "tracking" behaviour.

Accordingly, a new planiform optical laser recording with

(A) an electrically conductive, dimensionally stable carrier and with

(B) one or two amorphous, electrically conductive, thermally modifiable recording layer(s) lying facing each other with a cationic polymer that can be produced by electrolysis as one of the essential components was found,

which is characterised by the fact that the electrically conductive, dimensionally stable carrier (A),

(a_1) constitutes a band, a quadratic or rectangular plate or a round disc made from plastic and

(a_2) shows structures in the surface, which is turned to a recording layer (B), for which

(a_3) this surface is additionally covered with a 20 to 100 nm thick layer of Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au, Ni and/or Cu.

and that the amorphous, electrically conductive, thermally modifiable recording layer (B) or one each of the two recording layers (B) contains

(b_1) 30 to 95% by weight, with respect to (B), of a homopolymer of pyrrole, N-alkylpyrrol, N-arylpyrrole, thiophene or of aniline of a copolymer of at least two of these monomers or one copolymer of at least one of these monomers with furane and/or thiazole and

(b_2) 5 to 70% by weight, with respect to (B), of at least one anionic pigment made from the class of azo-, perylene-, anthaquinone-, cyanine-, phthalocyanine-, porphine-, tetraazaporphine-, hemiporphyrazine-, and/or tetrathiolato-metalcomplex-pigment.

The one essential component of the recording material, according to the invention, is the amorphous, electrically conductive, thermally modifiable recording layer (B), in which the pigments are bound to the polymer by ionic bonds. Further, according to the invention, the anionic pigments, i.e. pigments containing negative charges, are bound to the cationic polymer, i.e. polymer containing positive charges.

The main criterion for the selection of the suitable anionic pigments, according to the invention, is whether its maximum absorption lies close to the wavelength λ of the writing laser ray or is equal to this wavelength. Thus, while using a writing laser that emits wavelength in the visible range one selects a pigment with maximum absorption that falls precisely in this range, whereas while using a semiconductor laser one uses a pigment that absorbs in the IR range.

A further criterion for the selection of suitable anionic pigments is its solubility in liquid polar mediums. Solvents or solvent mixtures, which go into dipole-dipole-, dipole-ion-, or ion-ion-interactions within themselves or with the dissolved materials in them, like water, ethyl alcohol, acetonitrile, dioxane, N-methylprrolidone, propylenecarbonate, hexamethylphosphoric acid-triamide, dimethylsuphoxide or acetone, come under this category.

Anionic pigments, which originate from the classes of azo-, perylene-, anthraquinone-, cyanine-, phthalocyanine-, porphine-, tetraazaporphine-, hemiporphyrazine-, and/or tetrathiolato-metal complex-pigments, are well suited. Of these, derivatives the of phthalocyanine, porphine, tetraazaporphine, hemiporphyrazine, or of a tetrathiolato-metal complex are of advantage and derivatives of the phthalocyanine are of special advantage.

Well-suited anionic pigments contain known anionic groups in which carboxylate-, o-phosphate-, o-sulphate- or sulphonate groups are of advantage and sulphonate groups are of special advantage.

Examples of especially well-suited anionic pigments are therefore sulphonate-group-containing, metal-free or metal-containing phthalocyanine derivatives like phthalocyanine-mono- and –tetrasulphonate or sulphonated chrome-, manganese-, iron-, cobalt-, nickel-, palladium-, tin-, copper-, cadmium-, titanium-, vanadium-, niobium-, tantalum-, chloroaluminium-, hydroxoaluminium-, or silicon phthalocyanine complexes. These phthalocyanine derivatives can contain, besides sulphanate group(s), additional groups like halogen atoms or alkyl-, cycloalkyl-, ω-arylalkyl- or aryl-residues, in which the later can also be kata- or peri-anellated at the phenyl core of the phthalocyanine basic structure.

The recording layers (B) of the recording material, according to the invention, contain anionic pigment to the extent of 5 to 70, preferably 10 to 60 and especially 15 to 50% by weight with respect to the recording layer (B).

All electrically conductive polymers come into question for the build-up of the recording layer (B) of the recording materials according to the invention, as long as they contain cationic groups and can be produced by electrolysis from monomers soluble in liquid polar mediums.

Polymers, which contain ammonium- or ammonium-groups and/or a positively charged bonding system of several conjugated double bonds, are well suited.

Examples of especially well-suited cationic polymers are homopolymer of pyrrole or of N-alkyl- or N-arylpyrrolene; copolymer of these compounds with each other and /or with furan, thiophene or thiazolel; or homopolymer of thiophene or aniline; of which homopolypyrrole and copolymer of pyrrole are particularly advantageous. Further,

homopolypyrrole is especially most advantageous. These polymers are produced from the especially well-suited monomers of pyrrole, N-alkyl- or N-arylpyrrole, thiophene or aniline, for which, especially in the case of pyrrole monomers, furan, thiophene or thiazole come into consideration as comonomers.

The recording layers (B) of the recording material, according to the invention, contain cationic polymer to an extent of 30 to 95, preferably 40 to 90, and especially 50 to 85% by weight with respect to the recording layer (B). In addition to this, the recording layers contain further suitable additional materials like non-ionic pigments, non-ionic polymers, softener, antiozonant or anti-oxidants.

In general, the recording layers (B) are 0.001 to 1.5 μm thick.

Therefore, the especially advantageous recording materials, according to the invention, exhibit recording layers (B) in which 5 to 70% by weight with respect to the layer (B) of especially well-suited phthalocyanine derivatives containing sulphonate groups are linked with 95 to 30% by weight by polypyrrole through ionic bonds.

Another important component of the recording material, according to the invention, is the electrically conductive, dimensionally stable carrier (A). This carrier (A) can have the form of a band, quadratic or rectangular plate or a round disc. The round disc form is of advantage.

The carrier (A) holds one or two of the recording layers (B) described above in detail. If it carries two recording layers (B), then these lie facing each other, i.e. they are exposed to both the largest surfaces of the carrier (A). Carriers (A) that carry only one recording layer (B) are of advantage.

The carrier (A) exhibits structures on the surface that are to be turned into a recording layer (B). The structures on the surface lie in the micrometer and/or sub-micrometer range. They serve for the exact guidance of the reading laser ray and ensure fast and

accurate response of the track-servo and auto-focussing devices to the optical laser writing and reading heads of the commonly used disk-drive, i.e. they enable or improve tracking. Moreover, these structures themselves can be data, as is the case, for example, with well-known audio and video compact discs, or they can serve for the codification of entered data. The structures consist of projections and/or depressions. These are present in the form of continuous, concentric or spiral forming grooved tracks or as isolated hills and holes. Besides, the structure can have a more-or-less smooth waveform. Here, preference is given to the grooved tracks. They exhibit a right-angled saw-teeth type, v-forming or a trapezoidal type contour in the cross direction. In general, the depressions are designated as "grooves' and the raised portions as "lands". Of special advantage are grooved tracks with 50 to 200 nm deep and 0.4 to 0.8 μm broad "grooves" with 1 to 3 μm broad "land" in between.

The structures are created using usual and known methods for the production of the carrier (A) from plastics by form-processing methods like injection moulding.

The carrier (A), which exhibits one or two structured surfaces, consists of a plastic.

Especially well-suited carriers (A) consist of polymethylmethacrylate, polycarbonate, styrole/acrylnitrile-copolymer or a mixture of polystyrole and poly (2,6-dimethyl-phen-1,4-ylen-ether).

The structured surfaces of the carriers (A) are covered with a 20 to 100 nm, especially 40 to 80 nm thick layer made from Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au, Ni and/or Cu. Here, a layer made from Au is of special advantage.

The layer, which covers a structured surface of the carrier (A), serves as anode for the production of the recording layer (B) and, if necessary, as reflection layer in the production of recording material, according to the invention. It is produced as per usual and known methods of production of thin metal layers.

Especially advantageous planiform optical recording, according to the invention, consist of

(A) a round disc (a_1) made from polymethylmethacrylate, polycarbonate, polymethylpentene, styrole/acrylnitrile-copolymer or made from a mixture of polystyrole and poly (2,6-dimethyl-phene-1,4-ylene-ether) with

(a_2) a surface exhibiting tracks, which

(a_3) is covered by a 40 to 80 nm thick Au layer,

and

(B) a recording layer consisting of

(b_1) 40 to 90% by weight, especially 50 to 85% by weight, with respect to (B), of a homopolypyrrole and

(b_2) 10 to 60% by weight, especially 15 to 50% by weight, with respect to (B), of phthalocyanines, which carry one or more sulphonate groups.

In addition to this the recording materials, according to the invention, exhibit additional layers, e.g., protecting layers.

According to the invention, the recording layers (B) are produced electrochemically directly on the carriers (A) or on the metal layers lying on them.

With this, one uses solutions of the especially well-suited monomers in liquid polar mediums, which contain the above-mentioned anionic pigments as the sole conductive salt. These solutions are subjected to direct current electrolysis under electrostatic conditions, by which one produces on the anode, i.e., on the metal layers mentioned

above, an electrically conductive polymer film, which contains the anions of the pigment, from the monomers by anodic oxidation.

One obtains the particularly advantageous recording materials, according to the invention, by anodic oxidation of electrically conductive solutions, which have as monomer pyrrole and as conductive sodium salts of phthalocyanines containing sulphonate groups. In this case, the use of liquid polar mediums, which contain water, is of special advantage.

The recording materials, according to the invention, are written with analog or digital data by means of a writing laser ray, for which one uses, as is well known, for writing analog data, a continuous wave laser and, for writing digital data, a pulse-coded laser.

In general, suitable lasers exhibit a radiation power of 1 to 20 m Watt for the writing wavelength λ The focus diameter of the writing laser ray lies in general from 200 to 2000 nm. In general, the pulse duration for the radiation with a pulse-coded laser amounts to 10 to 1000 ns. One uses advantageously a laser ray of light of wavelength λ which is absorbed well by the recording layer concerned. Wavelengths λ of 400 to 1000 nm, especially 600 to 900 nm, are advantageous.

For the writing process, the writing laser ray is moved over the recording material in relative movement. Moreover, it hits the recording material vertically or is focussed on its recording layer (B). The recording layer (B) is heated locally at the place where it is hit and thermally modified areas arise, for example in the form of holes, craters or spots. These areas have essentially a round or oval form (spots) for writing data with pulse-coded lasers. They can have any form for writing with continuous wave laser.

The written data is read with the help of a reading laser ray. The radiation power of the laser for the reading wavelength λ' lies below the threshold power from which writing is possible. In general, the radiation power lies from 0.01 to 3 mWatt. One uses advantageously laser light of wavelength λ', which is well absorbed by the recording

layer, or of such wavelength λ', which is absorbed hardly or not at all. Wavelengths λ' of 400 to 1000 nm, especially 600 to 900 nm, are advantageous.

For this laser process too, the reading laser ray is moved over the recording material in relative movement. Moreover, it hits the recording material vertically or is focussed on its recording layer (B).

If the reading laser ray hits a thermally modified area while tracing over the recording layer (B) a spot, for example, then the properties of the transmitted or reflected light from the recording material changes. This can be detected with the help of a suitable detector.

For this, it is especially advantageous to use writing and reading lasers that radiate laser rays in the wavelengths in the region of 600 to 900 nm. Besides, it is of further particular advantage, if the writing wavelength λ is identical to the reading wavelength λ', or differs only minimally from it. Light of this wavelength is supplied by usual and well-known HeNe-lasers or by semiconductor lasers.

For optical laser writing and reading, the usual well-known optical laser disc drive can be used.

The recording materials, according to the invention, exhibit a number of exceptional advantages. Thus, its unwritten recording layer (B) is stable, so that it itself is still outstandingly suitable for optical laser writing and reading of data after long storage at comparatively higher temperature and humidity. The same applies to the written recording layer (B). Here also no information loss is encountered after very long storage. Beyond this, the recording layers (B) can be produced electrochemically especially advantageously, by which the formation of cracks and holes are avoided and the thickness and composition of the layers can be adjusted and reproduced exactly. These exceptional advantages accrue even though the surfaces, on which the recording layers (B) are separated, are structured. It is expected that some disadvantages could

result from this. The recording layers (B) open up new possibilities for application and further processing on the basis of their electrical conductivity. Thus, for example, additional layers can be laid on them electrochemically in the same way. Further, a recording density of above 10^6 to 10^8 bits per cm^2 and a constant high signal-noise-ratio is achieved for the recording materials according to the invention, whereby the data can also be read immediately after writing. In addition to this the recording materials, according to the invention, exhibit excellent "tracking" behaviour. Therefore, the recording materials are especially suited outstandingly for archiving purpose, according to the invention.

Example

Production, properties and use of recording materials according to the invention

A solution of 98.9% by weight water, 1% by weight pyrrole and 0.1% by weight of a phthalocyanine metal complex of a combination of phthalocyanine.$(SO_3Na)_{2,8}$.copper, with respect to the solution, was used for the production of recording layers (B).

Ten 13 cm diameter polycarbonate discs having grooved tracks, which were covered with a 50 nm thick layer of gold on one side (carrier A), were dipped into this solution. The metal layer served as anode for the electrolysis and as reflector layer in the finished recording materials. The recording layers (B) were produced on the metal layers of the carriers electrostatically by a current strength of 2 mA per cm^2 for 1 minute and subsequently dried.

The pigment content of the recording layers (B) was reckoned at 31% by weight, with respect to the layer, of copper and sulphur determined by chemical analysis. The refractive index of the layers was determined ellipsometrically with the help of a HeNe-laser with a wavelength of $\lambda = 632$ nm, at 1.4 to 1.6. The maximum absorption of the layers was between 600 to 700 nm, its coefficient of extinction K amounted to 0.6 to 0.8. All layers, in spite of the grooved tracks, were uniformly 0.8 μm thick and

exhibited conductivity of more than 10^{-1} S/cm. No crystallisation, holes or cracks were observed during microscopic examination.

Five of the recording materials were stored for 30 days at 60° C and a relative humidity of 90%. No disadvantageous changes were observed in the recording layers after that.

The remaining 5 recording materials were written immediately after their production with the help of a typical and known optical laser writing and reading device (disk-drive) with digital data in the form of holes. Here, a HeNe-laser was used, which radiated a wavelength $\lambda = 630$ nm and a light power of 15 mWatt. The pulse duration of the laser was 700 ns. The writing occurred from the side of the recording layers. All the slightly oval holes obtained in the recording layers in this way exhibited a maximum diameter of about 1.5 μm.

These recording materials were read immediately after writing with the HeNe-laser (wavelength $\lambda' = 632$ nm, light power = 2 mWatt) reduced in power. The light reflected from the recording materials was recorded with that. It was established that the data had been written practically error-free. The error-rate was under 1 error per 10^5 bits. The light signals reflected from the recording layers were very strong and undistorted.

These 5 recording materials were stored for 30 days at 60° C and a relative humidity of 90% and subsequently read afresh. No changes were found .

Writing and reading were repeated with the recording materials that were stored after production. It showed that storage did not cause any deterioration whatsoever. The stored recording materials also delivered good results like the ones that were written immediately after their production.

Example 2 and 3

Production, properties and use of recording materials according to the invention

Example 1 was repeated, except that a layer made from platinum (example 2) and a layer made from nickel (example 3) was used instead of a gold layer.

In both the cases, the results obtained were comparable to the full extent with those from example 1.